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**The following information has been drawn from the documents submitted by the applicant**

54 Process for the production of foam materials containing polyisocyanate polyaddition products

57 Process for the production of foam materials containing polyisocyanate polyaddition products by transformation of (a) polyisocyanates, (b) versus isocyanate reactive compounds with a molecular weight of 500 to 8,000 g/mole and possibly (c) chain elongating agents and/or cross linking agents with a molecular weight of less than 500 g/mole in the presence of foaming agents (d) and of catalysts (e) as well as possibly in the presence of (f) auxiliary materials and additives, thus characterized in that foaming agents are used containing hydrocarbons with $C_3$ or $C_4$ rings, exhibiting a boiling point between 0°C and 75°C at a pressure of 1,013 mbar.

Patent specifications

The invention concerns a process for the production of foam materials containing polyisocyanate polyaddition products by transformation of (a) polyisocyanates, (b) versus isocyanate reactive compounds with a molecular weight of 500 to 8,000 g/mole and possibly (c) chain elongating agents and/or cross linking agents with a molecular weight of less than 500 g/mole in the presence of foaming agents (d) and of catalysts (e) as well as possibly in the presence of (f) auxiliary materials and additives, and concerns the foam materials produced by this process as well. Furthermore, the invention relates to components containing foaming agents reacting with isocyanates and to the use of mixtures, containing hydrocarbons with $C_3$ or $C_4$ rings, which exhibit a boiling point between 0°C and 75°C at a pressure of 1,013 mbar, as foaming agents for the production of foam materials containing polyisocyanate polyaddition products.

The production of foamed materials, such as flexible foam, semi-rigid or rigid expanded/high resistance foams of an isocyanate base, by transformation of (a) polyisocyanates, (b) versus isocyanate reactive compounds with a molecular weight of 500 to 8,000 g/mole and possibly of (c) chain elongating agents and/or cross linking agents with a molecular weight of less than 500 g/mole in the presence of foaming agents (d) and of catalysts (e) as well as possibly in the presence of (f) auxiliary materials and additives is generally known, and is described, for example, in the "Plastics Handbook", volume 7, Polyurethanes, third edition, 1993, published by R. Vieweg and A. Höchtlen, Carl-Hanser Publishing Company, Munich.

The most important chemical starter materials are polyfunctional isocyanates. Chemical structures developing from these isocyanates can be polyurethanes, polyureas, polyisocyanurates, as well as other additional isocyanate adducts such as for example allophanates, biurets, carbodiimides and isocyanate adducts thereof, oxazolidones, polyimides, polyamides, whereby the type of structure obtained depends on the reaction partners of the isocyanates, and on the catalysis as well as on the reaction conditions. In general, polyisocyanate polyaddition products are subsumed under the concept of polyurethanes because polyurethanes constitute the most important and most frequently occurring material group for foamed materials of an isocyanate base.

As foaming agents for the production of polyurethane foam materials there are basically two types of foaming agents that are used:

low boiling, inert liquids that evaporate under the influence of the exothermic polyaddition reaction, preferably halogenated hydrocarbons such as methylene chloride, trichlorofluoro- methane among others, and chemical compounds that form propellant gases by a chemical reaction or by thermal decomposition. Let us name for example the transformation of water with isocyanates under formation of amines and carbon dioxide, which occurs in sync with polyurethane formation, and the separation of thermally labile compounds such as for example azo-iso-butyric acid nitrile, which yields toxic tetraethyl succinonitrile in addition to yielding nitrogen as a separation product, or azodicarbonamide, whose application as a component in a foaming agent combination is described in the patent EP-A-0 092 740 (CA 1 208 912). While the latter mentioned method, in which thermally labile compounds such as azo-compounds, hydrazides, semicarbazides, N-nitroso compounds, benzoxazines among others (Plastics 66 (1976)) are conventionally integrated into a pre-processed polymer, has maintained a minor role in its technical significance, the physically active, low boiling liquids have found worldwide application on a large scale as foaming agents for the production of polyurethane foams or polyisocyanurate foamed materials.

According to the information provided in the patent EP-A-351 614, the following can be used as foaming agents in the production of polyurethane foam materials: fluorinated hydrocarbons, perfluorinated hydrocarbons, sulfur hexafluoride or mixtures of at least two of these compounds. Because these fluorinated or perfluorinated foaming agents are difficult to dissolve or are insoluble in the formulation components for the production of polyisocyanate polyaddition products, they are emulsified in at least one organic and/or modified organic polyisocyanate, in at least one higher molecular compound with at least two reactive hydrogen atoms or in a mixture of at least one higher molecular compound with at least two reactive hydrogen atoms and with one low molecular chain extending agent and/or cross linking agent. By using this method, cellular plastics can be produced with a homogeneous and fine cellular structure. The drawback however, is the high price for these foaming agents. In order to obtain closed cell plastics with especially advantageous cellular structures, one must rely on a narrowly limited selection of mixtures consisting of perfluoropentane and perfluorohexane.

Furthermore, alkanes can be used as foaming agents such as butane and pentane among others. In the German patent DE-A-3 933 335, the use of cyclopentane is proposed.

In the EP-A-0 405 439 patent, the combination of perfluoro- alkanes with cyclo- alkanes is mentioned, whereby the cyclo- alkane content should be smaller than the moiety of perfluoro- alkane compound. The slight expanding action of this foaming agent mixture causes a high water content for the polyol component, which lies at above 3%. Polyurethanes produced in this manner are characterized by lower thermal insulation and poorer mechanical properties, in particular by greater brittleness and inferior adhesion, as compared to foamed materials produced with conventional foaming agents.

Cyclopentane, also in mixtures such as for example with highly and/or perfluorinated organic compounds or with (cyclo-) aliphatic compounds, is further described in the German patent DE-A-4 200 558 as a foaming agent for the production of rigid expanded foamed polyurethanes.

As compared to rigid polyurethanes foamed with trichlorofluoro- methane for example, poorer dimensional stability, due almost solely to out-diffusing action of the foaming agents, as well as increased thermal conductivity proved to be disadvantageous characteristics in rigid foams produced with the described foaming agents.

Therefore, the objective of the current invention was to develop a process for the production of polyurethane foam materials, in particular for rigid expanded foamed polyurethanes, in which foaming agents are used that lead to the production of foamed materials with a lower thermal conductivity and an improved dimensional stability, that is, for example with lesser shrinkage resulting from the out-diffusing action of the foaming agents.

The objective could be achieved by using foaming agents that contain hydrocarbons with $C_3$ or $C_4$ rings, exhibiting a boiling point between 0°C and 75°C, preferably between 10°C and 70°C, especially preferred between 20°C and 50°C, in particular between 25°C and 46°C and at a pressure of 1,013 mbar.

Furthermore, subject of the invention are components containing foaming agents that react with isocyanates, containing 5 to 25 weight percent in hydrocarbons with $C_3$ or $C_4$ rings, which exhibit a boiling point between 0°C and 75°C, preferably between 10°C and 70°C, especially preferred between 20°C and 50°C, in particular between 25°C and 46°C at a pressure of 1,013 mbar, and possibly compounds as well that homogeneously mix with the former, with a boiling point between - 40°C and + 100°C at a pressure of 1,013 mbar, 0.5 to 3 weight percent in water and 82 to 94.5 weight percent of the

components (b) and possibly (c) for the production of rigid expanded foamed polyurethanes.

As foaming agents (d), aliphatic cyclic compounds are preferably used with $C_3$ or $C_4$ rings and with a total of 4 to 7 carbon atoms, preferably with 5 or 6 carbon atoms: especially preferred are bicyclo [1.1.1] pentane, spiropentane, trans- 1,2- dimethyl cyclopropane, cis- 1,2- dimethyl cyclopropane, 1-methyl bicyclo [1.1.0] butane, ethyl cyclopropane, methyl cyclobutane and/or bicyclo [2.1.0] pentane.

The foaming agents in accordance with the invention for the production of rigid polyurethane foam materials are normally used in a quantity of 0.5 to 25 weight percent, preferably 5 to 15 weight percent relative to the component (b) applied for the production of the rigid polyurethane foam materials, that is, the higher molecular compound with at least two reactive hydrogen atoms.

In order to expand on the processing range in relation to the reaction parameters and the foaming equipment, and to increase processing safety together with a reduction of the formation of industrially unusable foam material wastage, the use of water as an additional foaming agent has proven to be advantageous in conjunction with the foaming agents (d), in accordance with the invention. Depending on the desired foam material density and the quantity of foaming agent mixture applied, the water content, relative to the component (b), expediently lies above 0.1 weight percent, preferably in the range between 0.5 to 3 weight percent.

The compounds in accordance with the invention can further be used as foaming agents in mixtures with compounds, with which they are entirely or partially homogeneously miscible, which have a boiling point between - 40°C and + 100°C at a pressure of 1,013 mbar. For example, linear and/or branched hydrocarbons can be used as entirely or partially homogeneously miscible compounds, such as cycloalkanes, preferably cyclopentane and/or highly fluorinated and/or perfluorinated hydrocarbons, in the mixtures with the foaming agents in accordance with the invention. For example, as fluorinated or perfluorinated compounds, the following come under consideration:

e.g., as fluorinated or perfluorinated compounds, one can use linear or cyclic ether with 4 to 12 carbon atoms, preferably 4 to 6 carbon atoms such as for example perfluoro - diethyl-, perfluoro-dipropyl- and perfluoro ethyl propyl ether, oligomers from perfluoro ethylene oxide, from perfluoro propylene oxide or mixed perfluoro ethylene - perfluoro propylene oxide as well as cyclic perfluoro ether such as for example perfluoro tetrahydrofuran or perfluoro alkyl tetrahydrofurans, and highly fluorinated or perfluorinated tertiary alkyl amines with 1 to 5 carbon atoms, preferably 2 to 4 carbon atoms in the alkyl radical such as for example perfluoro triethyl-, perfluoro tripropyl- or perfluoro tributyl amine, as well as gaseous aliphatic or cyclo-aliphatic perfluoro alkanes at room temperature, such as for example perfluoro propane, perfluoro butane or perfluoro cyclobutane, which are liquefied, mixed and emulsified under pressure e.g., at a pressure of up to about 25 bar.

As (per)- fluorinated and highly fluorinated hydrocarbons of this type, let us name a few examples: perfluoro pentane, perfluoro hexane, perfluoro heptane, perfluoro octane, perfluoro cyclopentane, perfluoro cyclohexane as well as hexafluoro propane and heptafluoro propane. For this, one preferably uses perfluoro pentane and especially perfluoro hexane as well as mixtures thereof. As fluorinated organic compounds such can be expediently applied which are predominantly, for example 85% fluorinated, and that have at least one, preferably only one combined hydrogen atom.

These possibly difficult to dissolve or insoluble (per)fluorinated organic compounds in the starter components for the rigid expanded foamed polyurethane production, which expediently exhibit a boiling

point maximum of 150°C, preferably of - 40°C to 100°C, especially preferably of 0°C to 90°C, or particularly of 10°C to 60°C at a pressure of 1,013 mbar, can be applied individually or together in the form of a mixture.

As hydrocarbons that are entirely homogeneously miscible with the foaming agents in accordance with the invention, one can use for example cycloalkanes with more than 4 carbon atoms in the ring, such as for example cyclohexane and preferably cyclopentane. Furthermore, the linear and/or branched alkanes with 4 to 8 carbon atoms, such as butane, pentane, hexane, heptane or octane come under consideration. Having proven themselves as particularly advantageous for this are the linear and/or branched alkanes with 5 or 6 carbon atoms, in particular n-pentane, iso-pentane, isomeric pentane mixtures or iso-hexane.

The production of polyurethane foam materials, in particular of rigid expanded foamed polyurethanes is carried out by transformation in a manner that is in and of itself known:

a) organic and/or modified organic polyisocyanates with
b) at least one compound with at least two reactive hydrogen atoms and a normal molecular weight of 500 to 8,000 g/mole and possibly
c) with chain elongating agents and/or cross linking agents with a molecular weight smaller than 500 g/mole in the presence of
d) the foaming agents in accordance with the invention as well as with
e) catalysts and possibly
f) with additional standard auxiliary agents and/or additives.

With the exception of the foaming agents (d), known formulation components are used for the production of rigid expanded foamed polyurethanes in accordance with the invention's process, concerning which the following must be elaborated:

a) As organic polyisocyanates, known aliphatic, aliphatic cyclic, aral- aliphatic and preferably aromatic polyvalent isocyanates come into consideration.

Let us name individually as examples: alkylene diisocyanates with 4 to 12 carbon atoms in the alkylene group such as 1,12- dodecane - diisocyanate, 2- ethyl - tetramethylene - diisocyanate - 1,4, 2- methyl - pentamethylene - diisocyanate - 1,5, tetramethylene - diisocyanate - 1,4 and preferably hexa-methylene - diisocyanate - 1,6; aliphatic cyclic diisocyanates such as cyclohexane - 1,3- and -1,4 - diisocyanate as well as various mixtures of these isomers, 1- isocyanato - 3,3,5 - trimethyl - 5- isocyanato-methyl - cyclohexane (isophorone - diisocyanate), 2,4- and 2,6- hexahydro - toluylene - diisocyanate as well as the corresponding isomeric mixtures, 4,4'-, 2,2'- and 2,4'- dicyclo - hexyl - methane - diisocyanate as well as the corresponding isomeric mixtures, and preferably aromatic diisocyanates and polyisocyanates such as for example 2,4- and 2,6- toluylene - diisocyanate and the corresponding isomeric mixtures, 4,4'-, 2,4'-, and 2,2' - diphenyl - methane - diisocyanate and the corresponding isomeric mixtures, mixtures of 4,4'- and 2,4'- diphenyl - methane - diisocyanates, polyphenyl - polymethylene - polyisocyanato, mixtures of 4,4'-, 2,4'- and 2,2'- diphenyl - methane - diisocyanates and polyphenyl - polymethylene - polyisocyanates (raw MDI) and mixtures of raw MDI (methylene diisocyanate) and toluylene diisocyanates. The organic diisocyanates and polyisocyanates can be applied individually or in the form of their mixtures.

So-called modified polyvalent isocyanates, that is, products obtained by chemical transformation of diisocyanates and/or polyisocyanates, can also frequently be used. Let us name as examples

diisocyanates and/or polyisocyanates that contain ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups. The following come under consideration individually: organic, preferably aromatic polyisocyanates containing urethane groups, with NCO contents of 33.6 to 15 weight percent, preferably from 31 to 21 weight percent relative to the total weight, for example with low molecular diols, triols, dialkylene glycols, trialkylene glycols or polyoxy - alkylene glycols with molecular weights of up to 6,ooo, in particular with molecular weights of up to 1,500, modified 4,4'-diphenyl methane diisocyanate, modified 4,4'- and 2,4'- diphenyl methane diisocyanate mixtures, or modified raw MDI or 2,4- or 2,6- toluylene diisocyanate, whereby the dioxy - alkylene glycols or polyoxy - alkylene glycols can be used individually or as mixtures, for example, let us name: diethylene- glycol, dipropylene glycol, polyoxy - ethylene-, polyoxy propylene and polyoxy propylane - polyoxy ethylene - glycols, - triols and/or -tetrols. Also suitable are NCO group containing prepolymers with NCO contents of 25 to 3.5 weight percent, preferably from 21 to 14 weight percent relative to the total weight, produced from the subsequently described polyester- polyols and/or preferably from the polyether polyols and 4,4' - diphenyl methane - diisocyanate, from mixtures composed of 2,4'- and 4,4'- diphenyl methane - diisocyanate, from 2,4- and/or 2,6 - toluylene diisocyanates or from raw MDI. Furthermore, liquid carbodiimide groups and/or isocyanurate ring containing polyisocyanates with NCO contents from 33.6 to 15, preferably from 31 to 21 weight percent relative to the total weight, for example on the basis of 4,4'-, 2,4'- and/or 2,2- diphenyl methane - diisocyanate and/or 2,4- and/or 2,6- toluylene - diisocyanate have proven to be useful.

The modified polyisocyanates can possibly be mixed with one another or with unmodified organic polyisocyanates such as for example 2,4'-, 4,4' diphenyl - methane - diisocyanate, raw MDI, 2,4- and/or 2,6- toluylene - diisocyanate.

Especially time-tried as organic polyisocyanates and therefore preferably applied are: mixtures of toluylene- diisocyanates and raw MDI or mixtures of modified urethane group containing organic polyisocyanates with an NCO content from 33.6 to 15 weight percent, in particular such that are of a base of toluylene diisocyanates, 4,4'- diphenyl methane diisocyanate, diphenyl methane diisocyanate isomeric mixtures or raw MDI and in particular raw MDI with a diphenyl methane diisocyanate isomeric content from 30 to 80 weight percent, preferably from 30 to 55 weight percent.

b) Expediently used as higher molecular compounds “b)” with at least two reactive hydrogen atoms are those with a functionality of 2 to 8, preferably of 2 to 6, and with a molecular weight of normally 500 to 8,000, preferably of 1,200 to 6,000. The following have proven to be useful, for example, polyether - polyamine and/or preferably polyols selected from the group of polyether - polyols, of polyester - polyols, of polythioether - polyols, of polyester amides, of hydroxyl group containing polyacetals and hydroxyl group containing aliphatic polycarbonates or mixtures of at least two of the named polyols. Preferably applied are polyester polyols and/or polyether - polyols. The hydroxyl number of the polyhydroxyl compounds thereby amounts to 150 through 850 as a rule, and preferably to 200 through 600.

Suitable polyester - polyols can, for example, be produced from organic dicarboxylic acids with 2 to 12 carbon atoms, preferably from aliphatic dicarboxylic acids with 4 to 6 carbon atoms, and from polyvalent alcohols, preferably from diols, with 2 to 12 carbon atoms, but preferably with 2 to 6 carbon atoms. As dicarboxylic acids, the following examples come under consideration: succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decane - dicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid. For this, the dicarboxylic acids can be used individually as well as in a mixture with one another. Instead of the free dicarboxylic acids, the

corresponding dicarboxylic acid derivatives can also be used, such as for example, dicarboxylic acid esters from alcohols with 1 to 4 carbon atoms or dicarboxylic acid anhydrides. Preferably used are dicarboxylic acid mixtures from succinic, glutaric and adipic acids in a quantitative ratio of 20 to 35:35 to 50:20 to 32 weight parts, and specifically used is adipic acid. Examples for divalent or polyvalent alcohols, in particular for diols are: ethane diol, diethylene glycol, 1,2- or 1,3- propanediol, dipropylene glycol, 1,4- butanediol, 1,5- pentanediol, 1,6- hexanediol, 1,10- decanediol, glycerin and trimethylol propane. Preferably used are ethanediol, diethylene glycol, 1,4- butanediol, 1,5- pentanediol, 1,6- hexanediol or mixtures of at least two of the mentioned diols, in particular mixtures from 1,4- butanediol, 1,5- pentanediol and 1,6- hexanediol. Furthermore, polyester polyols from lactones can be used, such as for example ϵ-caprolactone or hydroxy - carboxylic acids, for example ω- hydroxy - caproic acid.

For the production of polyester polyols, the following can be polycondensed: organic, for example aromatic and preferably aliphatic, polycarboxylic acids and/or derivatives and polyvalent alcohols, free of catalysts, or preferably in the presence of esterification catalysts, expediently in an atmosphere of inert gas such as for example nitrogen, carbon monoxide, helium, argon among others, in a melt at temperatures of 150°C to 250°C, preferably at 180°C to 220°C, possibly under reduced pressure until the desired acid number is obtained, which is advantageously smaller than 10, preferably smaller than 2. According to a preferred form of implementation, the esterification mixture is polycondensed at the above mentioned temperatures and brought to an acid number of 80 to 30, preferably of 40 to 30, under normal pressure and subsequently under a pressure of less than 500 mbar, preferably from 50 to 150 mbar. As esterification catalysts the following examples of catalysts come under consideration: iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metals, metal oxides or metal salts. Polycondensation can however be conducted in the liquid phase as well, in the presence of diluting agents and/or entrainers such as for example benzene, toluene, xylene or chlorobenzene for the azeotropic distillation of condensation water.

For the production of polyester polyols, the organic polycarboxylic acids and/or derivatives and polyvalent alcohols are expediently polycondensed in a molar ratio of 1:1 through 1.8, preferably of 1:1.05 to 1.2.

The obtained polyester polyols display preferably a functionality of 2 to 4, in particular of 2 to 3, and a molecular weight of normally 500 to 3,000, preferably of 1,200 to 3,000 and in particular of 1,800 to 2,500.

Especially used as polyols are polyether polyols however, which are produced according to known processes, for example by anionic polymerization with alkali hydroxides such as for example sodium hydroxide or potassium hydroxide or alkali alkoxides such as for example sodium methylate, sodium- or potassium methylate or potassium isopropylate as catalysts and by addition of at least one starter molecule which contains 2 to 8, preferably 2 to 6 combined reactive hydrogen atoms, or by cationic polymerization with Lewis acids such as antimony pentachloride, boron fluoride etherate among others, or bleaching clay as catalysts from one or several alkylene oxides with 2 to 4 carbon atoms in the alkylene group.

Suitable alkylene oxides are, for example, tetrahydrofuran, 1,3- propylene oxide, 1,2- or 2,3- butylene oxide, styrene oxide and preferably ethylene oxide and 1,2- propylene oxide. The alkylene oxides can be used individually, alternated in succession, or used as mixtures. As starter molecules, the following come under consideration for example: water, organic dicarboxylic acids such as succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic diamines, possibly N-mono-, N,N-

and N,N'- dialkyl substituted diamines with 1 to 4 carbon atoms in the alkyl radical such as possibly mono-substituted and dialkyl substituted ethylene diamine, diethylene triamine, triethylene tetramine, 13,- propylene diamine, 1,3- or 1,4- butylene diamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6- hexamethylene diamine, phenylene diamine, 2,3-, 2,4- and 2,6- toluylene diamine and 4,4'-, 2,4'- and 2,2'- diamino - diphenyl methane.

Further starter molecules coming under consideration are: alkanol amines such as for example ethanolamine, N-methyl- ethanolamine and N-ethyl- ethanolamine, dialkanolamine such as for example diethanolamine, N- methyl- diethanolamine and N- ethyl- ethanolamine, and trialkanolamine such as for example triethanolamine and ammonia. Preferably used are polyvalent, specifically divalent and/or trivalent alcohols such as ethanediol, propanediol-1,2 and -1,3, diethylene glycol, dipropylene glycol, butanediol-1,4, hexanediol-1,6, glycerin, trimethylol propane, pentaerythritol, sorbitol and saccharose.

The polyether - polyols, preferably polyoxy- propylene- polyols and polyoxy- propylene - polyoxy- ethylene - polyols have a functionality of preferably 2 to 6 and in particular of 2 to 4 and normally a molecular weight of 500 to 8,000, preferably of 1,200 to 6,000 and in particular of 1,800 to 4,000, and suitable polyoxy-tetramethylene - glycols have a molecular weight of up to about 3,500.

Furthermore, suitable as polyether- polyols are polymer-modified polyether- polyols, preferably graft polyether- polyols, in particular such that are of a styrene base and/or of an acrylonitrile base, which are produced by in situ polymerization of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile, for example at a weight ratio from 90:10 to 10:90, preferably 70:30 through 30:70, in an expedient manner as mentioned above for the polyether polyols and in analogy to the specifications of the German patents 11 11 394, 12 22 669 (US patents 3 304 273, 3 383 351, 3 523 093), 11 52 536 (GB patent 10 40 452) and 11 52 537 (GB patent 987 618), as well as [are suitable] polyether- polyol dispersions, which as a disperse phase, normally at a quantity of 1 to 50 weight percent, preferably 2 to 25 weight percent, contain: for example polyureas, polyhydrazides, combined tertiary amino group containing polyurethanes and/or melamine and which are described, for example, in the patents EP-B-011 752 (US patent 4 304 708), US-A-4 374 209 and DE-A-32 31 497.

Just as the polyester- polyols, the polyether- polyols can be used individually or in the form of mixtures. Furthermore, they can be mixed with the graft polyether- polyols or with the polyester polyols as well as with the hydroxyl group containing polyester amides, polyacetals, polycarbonates and/or polyether- polyamines.

Coming under consideration as hydroxyl group containing polyacetals are, for example, the compounds produced from glycols such as diethylene glycol, triethylene glycol, 4,4'- dihydroxy- ethoxy- diphenyl- dimethyl- methane, hexanediol and formaldehyde. Suitable polyacetals can also be produced by polymerization of cyclic acetals.

As polycarbonates exhibiting hydroxyl groups, such types come into consideration that are in and of themselves known and which can be produced, for example, by transformation of diols such as propanediol- (1,3), butanediol- (1,4) and/or hexanediol- (1,6), diethylene glycol, triethylene glycol or tetraethylene glycol with diaryl- carbonates such as, for example, diphenyl carbonate or phosgene.

Included under the polyester amides are, for example, the predominantly linear condensates which are obtained from polyvalent, saturated and/or unsaturated carboxylic acids or from anhydrides thereof, and from polyvalent saturated and/or unsaturated amino alcohols or from mixtures of polyvalent

alcohols and amino- alcohols and/or polyamines.

Suitable polyether- polyamines can be produced from the above mentioned polyether- polyols according to a known process. Let us name as examples the cyano- alkylation of polyoxy- alkylene- polyols and subsequent hydrogenation of the formed nitrile (US patent 3 267 050) or the partial or complete amination of polyoxy- alkylene- polyols with amines or ammonia in the presence of hydrogen and catalysts (German patent DE 12 15 373).

Especially time-tried as polyol compounds, and therefore used by preference, are the mixtures that expediently contain:

bi) 0 to 95 weight parts, preferably 20 to 80 weight parts of a polyether- polyol, started with sucrose, with a hydroxyl number of 300 to 500, preferably of 350 to 450, on the basis of 1,2- propylene oxide or of 1,2- propylene oxide and ethylene oxide,
bii) 0 to 95 weight parts, preferably 20 to 80 weight parts of a polyether- polyol, started with sorbitol, with a hydroxyl number of 400 to 600, preferably of 450 to 550, on the basis of 1,2- propylene oxide or of 1,2- propylene oxide and ethylene oxide,
biii) 0 to 20 weight parts, preferably 5 to15 weight parts of a polyether- polyol, started with ethylene diamine, with a hydroxyl number of 700 to 850, preferably of 750 to 800, on the basis of 1,2- propylene oxide,
biv) 0 to 60 weight parts, preferably 5 to 40 weight parts of a polyether- polyol, with a hydroxyl number of 400 to 600, preferably of 450 to 550, on the basis of 1,2- propylene oxide or of 1,2- propylene oxide and ethylene oxide, produced by using a mixture of sucrose and triethanolamine at a weight ratio of 1:2 through 2:1 as starter molecules and
bv) 0 to 40 weight parts, preferably 10 to 30 weight parts of a polyether- polyol, started with TDA, with a hydroxyl number of 300 to 500, preferably of 350 to 450, on the basis of 1,2- propylene oxide and ethylene oxide, with the determination that the sum of the weight parts of the components bi) through bv) does not exceed 100.

The rigid expanded foamed polyurethanes can be produced without using or while using chain elongating agents and/or cross linking agents. However, for the purpose of modifying the mechanical properties, for example hardness, the addition of chain elongating agents, cross linking agents or possibly of mixtures thereof can prove to be advantageous.

As chain elongating agents and/or cross linking agents, diols and/or triols are used with molecular weights of less than 500, preferably of 60 to 300. Coming into consideration are, for example, aliphatic, aliphatic cyclic and/or aral- aliphatic diols with 2 to 14, preferably 4 to 10 carbon atoms such as for example ethylene glycol, propanediol- 1,3, decanediol- 1,10, o-, m-, p- dihydroxy cyclohexane, diethylene glycol, dipropylene glycol and preferably butanediol- 1,4, hexanediol- 1,6 and bis- (2- hydroxy- ethyl)- hydroquinone, triols such as 1,2,4-, 1,3,5- trihydroxy- cyclohexane, glycerin and trimethylol propane and low molecular hydroxyl group containing polyalkylene oxides on the basis of ethylene and/or 1,2- propylene oxide and of the above mentioned diols and/or triols as starter molecules.

To the extent chain elongating agents, cross linking agents or mixtures thereof are used for the production of rigid expanded foamed polyurethanes, they must be expediently applied in a quantity of 0 to 20 weight percent, preferably of 2 to 8 weight percent relative to the weight of the polyol compound (b).

The foaming agent mixtures, in accordance with the invention as previously described, as well as the homogeneously miscible compounds possibly mixed together with them, with a boiling point between - 40°C and + 150°C, preferably between - 40°C and 100°C, especially preferred between 10°C to 60°C at a pressure of 1,013 mbar, for example aliphatic and/or aliphatic cyclic hydrocarbons and/or highly fluorinated and/or perfluorinated compounds are preferably dissolved or emulsified, for processing in accordance with the invention's process, in the formulation components (a), (b), or in mixtures of (b) and (c), or of (a) and (b). In order to obtain such foaming agent containing emulsions, emulsifiers which are known in polyurethane chemistry are suitable. Specifically used emulsifiers are oligomeric acrylates which contain combined groups of polyoxyalkylenes and aliphatic fluorocarbons as side groups and which exhibit a fluorine content of approximately 5 to 30 weight percent. Oligomeric acrylates of this type are sufficiently known in plastics chemistry (compare to patent EP-A-351 614 among others).

The oligomeric acrylates which are suitable as exemplary emulsifiers with polyoxy alkylene groups and with aliphatic fluorocarbon groups as side groups are expediently applied at a quantity of 0.01 to 6 weight parts, preferably of 0.2 to 3.5 weight parts and specifically of 0.5 to 2.0 weight parts relative to 100 weight parts of the formulation components (a), (b) or of the mixture from (b) and (c).

For the emulsification of the foaming agent mixture (d), as already previously explained, the organic and/or modified organic polyisocyanates (a) and the higher molecular compounds with at least two reactive hydrogen atoms (b) are suitable. Furthermore, mixtures from (b) and low molecular chain elongating agents and/or cross linking agents are suitable.

When using organic and/or modified organic polyisocyanates (a) as alternate emulsion phase, aromatic polyisocyanates are preferably used selected from the group of 2,4-, 2,6- toluylene- diisocyanate or from mixtures of the named isomers, 4,4'-, 2,4'- and 2,2'- diphenyl methane diisocyanate or mixtures from at least two of the named isomers and mixtures from diphenyl methane diisocyanates and polyphenyl- polymethylene- polyisocyanates. To the extent the organic polyisocyanates are crystalline at room temperature, they become liquefied by being mixed with liquid polyisocyanates and/or by suitable partial modification such as for example carbodiimidization and/or urethanization.

As alternate emulsion phase, higher molecular compounds are preferably applied with at least two reactive hydrogen atoms (b). Particularly well suited are polyester- polyols or mixtures thereof with a functionality of 2 to 3 and with a molecular weight of 480 to 3,000 and polyether- polyols or mixtures thereof with a functionality of 2 to 6 and with a molecular weight of 400 to 8,000, whereby the latter are expediently selected from the group of polyoxy ethylene polyols, polyoxy propylene polyols, polyoxy propylene - polyoxy ethylene polyols and polyoxy tetramethylene- glycols or mixtures thereof.

Particularly time-tried as foaming agent containing solutions or emulsions are such which contain:

5 - 25 weight percent of one of the above described foaming agent mixtures in accordance with the invention, containing hydrocarbons with $C_3$ or $C_4$ rings, which exhibit a boiling point between 0°C and 75°C at a pressure of 1,013 mbar as well as possibly compounds that are homogeneously miscible with these, with a boiling point between - 40°C and 150°C, preferably between - 40°C to 100°C, especially preferred between 0°C and 90°C, in particular between 10°C and 60°C at a pressure of 1,013 mbar,

0 - 5 weight percent, preferably 0.5 to 9 weight percent of water and 82 to 94.5 weight percent at least of a compound with at least two reactive hydrogen atoms (b) or mixtures from (b) and chain elongating

agents and/or cross linking agents (c) as well as possibly with an emulsifier.

For the production of solutions or emulsions containing foaming agents, the formulation components (a) or (b) or the mixtures from (b) and (c) and the foaming agent mixture (d) are intensely mixed together, and expediently so in the presence of an emulsifier, preferably of an oligomeric acrylate at temperatures between 0°C and 70°C, preferably between 20°C and 40°C. As suitable mixing equipment for this, let us name some examples: static mixers such as for example the SMX by the Sulzer Company (Switzerland) or dynamic mixers such as for example the propeller stirrer or Ultra-Turrax© by the Hanke and Kunkel Company (FRG).

c) As catalysts (e) for the production of rigid expanded foamed polyurethanes, compounds are used in particular which highly accelerate the reaction of the component (b) compounds containing reactive hydrogen atoms, or hydroxyl groups in particular, and possibly (c) the reaction with the organic, possibly modified polyisocyanates (a). Coming under consideration are organic metal compounds, preferably organic tin compounds such as tin- (II)- salts from organic carboxylic acids such as for example tin- (II)- acetate, tin- (II)- octoate, tin- (II)- ethyl hexoate and tin- (II)- laurate and the dialkyl tin- (IV)- salts from organic carboxylic acids such as for example dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin maleate and dioctyl tin diacetate. The organic metal compounds are applied alone or preferably in combination with strong basic amines. As examples let us name amidines such as 2,3-dimethyl- 3,4,5,6-tetrahydro- pyrimidine, tertiary amines such as triethyl amine, tributyl amine, dimethyl benzyl amine, N- methyl-, N- ethyl-, N- cyclohexyl morpholine, N,N,N',N'- tetramethyl ethylene diamine, N,N,N',N'- tetra- methyl butane diamine, N,N,N',N'- tetramethyl hexane diamine-1,6, pentamethyl- diethylene triamine, tetramethyl- diamino ethyl ether, bis- (dimethyl amino propyl)- urea, dimethyl piperazine, 1,2- dimethyl- imidazole, 1- aza- bicyclo- (3,3,0)- octane and preferably 1,4- diaza-bicyclo- (2,2,2)- octane and alkanolamine compounds such as triethanolamine, triisopropanolamine, N-methyl- diethanolamine and
N- ethyl- diethanolamine and dimethyl ethanolamine.

Furthermore, the following come under consideration as catalysts: tris- (dialkyl amino alkyl)- s-hexahydrotriazine, in particular tris- (N,N- dimethyl amino propyl)- s- hexahydrotriazine, tetra- alkyl ammonium hydroxide such as tetra- ethyl ammonium hydroxide, alkali hydroxides such as sodium hydroxide and alkali alkoxides such as sodium methylate and potassium isopropylate, as well as alkali salts from long chain fatty acids with 10 to 20 carbon atoms and possibly side standing OH- groups. Preferably, one uses 0.001 to 5 weight percent, in particular 0.05 to 2 weight percent of catalyst or catalyst combination relative to the weight of the component (b).

Auxiliary agents and/or additives (f) can also possibly be integrated into the reaction mixture for the production of rigid expanded foamed polyurethanes. As examples, let us name surface active substances, foam stabilizers, cellular regulators, filling agents, dyestuff, pigments, flame proofing agents, hydrolysis preventing agents, fungistatic and bacteriostatic acting substances.

As surface active substances, for example, such compounds come into consideration which serve to support the homogenization of the starter materials and which are also possibly suited for regulating the cellular structure of the plastics. As examples, let us name emulsifiers such as the sodium salts from castor oil sulfates, or from fatty acids as well as salts from fatty acids with amines, for example oleic diethyl amine, stearic diethanol amine, ricinoleic diethanolamine, salts from sulfonic acids such as for example alkali or ammonium salts from dodecyl benzene- or dinaphthyl methane disulfonic acid and ricinoleic acid; foam stabilizers such as siloxane - oxalkylene- mixed polymers and other organo-polysiloxanes, ethoxylated alkyl phenols, ethoxylated fatty alcohols, paraffin oils, castor oil esters or

ricinoleic acid esters, Turkish red oil and peanut oil, and cellular regulators such as paraffins, fatty alcohols and dimethyl polysiloxanes. Furthermore, to improve the emulsifying action, cellular structure and/or stabilization of the foam, the above described oligomeric acrylates with polyoxyalkylene groups and aliphatic fluorocarbon groups are suitable as side groups. The surface active substances are normally applied in quantities of 0.01 to 5 weight parts relative to 100 weight parts of the component (b).

By filling agents, especially acting as reinforcing filling agents, we understand those known standard organic and inorganic filling agents, reinforcing agents, weighting agents, agents for the improvement of abrasion resistance in paint, coating materials etc. As examples, let us name individually the following: inorganic filling agents such as siliceous minerals, for example layer silicates such as antigorite, serpentine, hornblende, amphibole, chrysotile, talcum; metal oxides such as kaolin, aluminum oxides, titanium oxides and iron oxides; metal salts such as chalk, barium sulfate and inorganic pigments such as cadmium sulfide, zinc sulfide as well as glass among others. Preferably used are kaolin (China clay), hydrous alumina silicate and co-sediments from barium sulfate and hydrous aluminum silicate as well as natural and synthetic fibrous minerals such as wollastonite, metal fibers and in particular glass fibers of various lengths, which possibly can be smoothed. As organic filling agents, the following examples come into consideration: coal, melamine, colophony, cyclopentadienyl resins and graft polymers such as cellulose fibers, polyamide fibers, polyacrylonitrile fibers, polyurethane fibers and polyester fibers on the basis of aromatic and/or aliphatic dicarboxylic acid esters and specifically on the basis of carbon fibers.

The inorganic and organic filling agents can be used individually or as mixtures and are advantageously integrated into the reaction mixture in quantities of 0.5 to 50 weight percent, preferably of 1 to 40 weight percent relative to the weight of the components (a) through (e), whereby the content in mats, felts and textures made of natural and synthetic fibers can reach values of up to 80.

Suitable flame proofing agents are for example tricresyl phosphate, tris- (2-chloro-ethyl)-phosphate, tris- (2- chloro- propyl)- phosphate, tris- (1,3- dichloro- propyl)- phosphate, tris- (2,3-dibromo- propyl)- phosphate, tetrakis- (2- chloro- ethyl) ethylene diphosphate, dimethyl methane phosphonate, diethanolamine methyl phosphonic acid diethyl ether as well as commercially available halogen containing flame proofing polyols.

Except for those already mentioned halogen substituted phosphates, inorganic or organic flame proofing agents can also be used such as red phosphorus, hydrated aluminum hydroxide, antimony trioxide, arsenic oxide, ammonium polyphosphate and calcium sulfate, expanded graphite or cyanuric acid derivatives such as for example melamine, or mixtures from at least two flame proofing agents such as for example ammonium polyphosphates and melamine as well as possibly corn starch or ammonium polyphosphate, melamine and expanded graphite and/or possibly aromatic polyesters for flame proofing of polyisocyanate - polyaddition products. In general, it has proven to be expedient to use 5 to 50 weight parts, preferably 5 to 25 weight parts of the above mentioned flame proofing agents for respectively 100 weight parts of component (b).

More detailed analysis of the above mentioned standard auxiliary materials and additives can be found in the reference literature, for example in the monograph by J. H. Saunders and K. C. Frisch "High Polymers", volume XVI, Polyurethanes, parts 1 and 2, Interscience Publishers, 1962 or 1964, or in the "Plastics Handbook", Polyurethane, volume VII, Hanser Publishing Company, Munich, Vienna, 1st and 2nd edition, 1966 and 1983.

For the production of rigid expanded foamed polyurethanes, the organic polyisocyanates (a), higher molecular compounds with at least two reactive hydrogen atoms (b) and possibly chain elongating agents and/or cross linking agents (c) are brought to react in such quantities that the equivalence ratio of the NCO groups of the polyisocyanates (a) to the sum of the reactive hydrogen atoms of component (b) and possibly of component (c) amounts to 0.85 to 1.25:1, preferably to 0.95 to 1.15:1 and especially to 1 to 1.05:1. In the event the rigid expanded foamed polyurethanes contain at least partially combined isocyanurate groups, then a ratio of the NCO groups of the polyisocyanates (a) to the sum of the reactive hydrogen atoms of component (b) and possibly of component (c) is normally applied amounting from 1.5 to 60:1, preferably from 1.5 to 8:1.

The rigid expanded foamed polyurethanes are advantageously produced in accordance with the one shot process, for example with the help of high pressure or low pressure technology in open or closed molding machines, for example in metallic molding machines.

What has proven to be particularly advantageous is processing according to the two component process and to integrate the formulation components (b), (d), (e) and possibly (c) and (f) in component (A) and to use the organic polyisocyanates, modified polyisocyanates (a) or the mixtures from the named polyisocyanates and possibly the foaming agents (d) as component (B).

The starter components are mixed at a temperature of 15°C to 90°C, preferably of 20°C to 60°C and in particular from 20°C to 35°C and are introduced either into the open molding machine, or possibly under elevated pressure, into the closed molding machine. As was previously described, mixing can be carried out mechanically by means of a stirrer or of a paddle screw. The molding machine temperature expediently ranges from 20°C to 110°C, preferably from 30°C to 60°C and specifically from 45°C to 50°C.

The rigid expanded foamed polyurethanes or solid mold foamed plastics produced in accordance with the process of the invention display, as a rule, a density of 0.02 to 0.75 g/cm3, preferably from 0.025 to 0.24 g/cm3 and in particular from 0.03 to 0.1 g/cm3. They are especially well suited as insulating materials in the construction industry and for household refrigerators, for example as heat insulation in refrigerating and/or heating appliances, sandwich elements or pipe lines.

The improved dimensional stability of the foam materials, according to the invention, with low thermal conductivity shall be illustrated by the following examples.

Example 1 (comparison)

Mixture of

Component A
60.3 parts polyol, produced from 25.2 parts sorbitol and
74.8 parts propylene oxide with KOH as catalyst and
0.5 parts water as co-starter. The hydroxyl number (OH number or OHZ) amounts to 495 mg KOH/g; the viscosity at 25°C is 17,900 mPas,
24.1 parts polyol, produced from a 22.7% mixture of 2,3- and 3,4- toluylene diamine, 28% ethylene oxide and 72% propylene oxide with KOH as catalyst. The OHZ amounts to 406 mg KOH/g; the viscosity at 25°C is 8,500 mPas,
2.3 parts water
1.5 parts of B 8423 stabilizer by the Goldschmidt Company
0.8 parts dimethyl cyclohexyl amine
11.0 parts cyclopentane
and

Component B
144 parts of B-component, a mixture of diphenyl methane diisocyanate and polyphenyl polymethylene - polyisocyanates (M 20 A by BASF Schwarzheide GmbH) with an NCO content of 31.5 weight %.

Component A was produced by mixing together the named substances into a homogeneous mixture.

46.0 g of polyisocyanate (B component) was mixed with 32.0 g of component A by a laboratory agitator, which was equipped with an agitator by the Vollrath Company, in a polystyrene bowl (diameter of 115 mm), at a speed of 1,750 revolutions per minute.

After foaming, thermal conductivity was measured on test pieces with a diameter of 80 mm and a thickness of 20 mm.

Additional test pieces with dimensions of 5 cm x 5 cm x 5 cm were used to determine raw density by dimensional measurement and weighing.

Resistance to shrinking was then measured on the above mentioned cubes under the following conditions:
The test pieces were stored at room temperature for 14 days and were subsequently stress tested with a uniaxial compressive stress of 0.05 N/mm2 for over 50,000 minutes. Deformation is a measure of mechanical stability, for example against negative pressure which is created by the CO2 diffused out of the foam. Shrinking behavior is improved if deformation is reduced at the same rate of density or when deformation is not increased at a lower rate of density.

Example 2 (in accordance with the invention)

The same as example 1, but instead of 11.0 parts of cyclopentane, 11.0 parts of spiropentane.

Example 3 (in accordance with the invention)

The same as example 1, but instead of 11.0 parts of cyclopentane, 11.0 parts of ethyl cyclopropane.

Example 4 (in accordance with the invention)

The same as example 1, but instead of 11.0 parts of cyclopentane, 11.0 parts of trans- 1,2- dimethyl-cyclopropane.

Example 5 (in accordance with the invention)

The same as example 1, but instead of 11.0 parts of cyclopentane, 11.0 parts of cis- 1,2- dimethyl-cyclopropane.

Example 6 (comparison)

Mixture of

Component A
63.2 parts polyol, produced from 25.2 parts sorbitol and 74.8 parts propylene oxide with KOH as catalyst and 0.5 parts water as co-starter. The hydroxyl number (OH number or OHZ) amounts to 495 mg KOH/g; the viscosity at 25°C is 17,900 mPas.
25 parts polyol, produced from a 22.7% mixture of 2,3- and 3,4- toluylene diamine, 28% ethylene oxide and 72% propylene oxide with KOH as catalyst. The OHZ amounts to 406 mg KOH/g; the viscosity at 25°C is 8,500 mPas.
3.5 parts water
1.5 parts of B 8423 stabilizer by the Goldschmidt Company
0.8 parts dimethyl cyclohexyl amine
6.0 parts cyclopentane
and
160 parts of component B, a mixture of diphenyl methane diisocyanate and polyphenyl polymethylene - polyisocyanates (M 20 A by BASF Schwarzheide GmbH) with an NCO content of 31.5 weight %.

Component A was produced by mixing together the named substances into a homogeneous mixture.

48.0 g of polyisocyanate (B component) was mixed with 30.0 g of component A by a laboratory agitator, which was equipped with an agitator by the Vollrath Company, in a polystyrene bowl (diameter of 115 mm), at a speed of 1,750 revolutions per minute.

After foaming, thermal conductivity was measured on test pieces with a diameter of 80 mm and a thickness of 20 mm.

Additional test pieces with dimensions of 5 cm x 5 cm x 5 cm were used to determine raw density by dimensional measurement and weighing.

Resistance to shrinking was then measured on the above mentioned cubes under the following conditions: The test pieces were stored at room temperature for 14 days and were subsequently stress tested with a uniaxial compressive stress of 0.05 N/mm2 for over 50,000 minutes. Deformation is a measure of mechanical stability, for example against negative pressure which is created by the CO2 diffused out of the foam.

Shrinking behavior is improved, if deformation is reduced at the same rate of density or when

deformation is not increased at a lower rate of density.

Example 7 (in accordance with the invention)

The same as example 6, but instead of 6.0 parts of cyclopentane, 6.0 parts of spiropentane.

Example 8 (in accordance with the invention)

The same as example 6, but instead of 6.0 parts of cyclopentane, 6.0 parts of ethyl cyclopentane.

Example 9 (in accordance with the invention)

The same as example 6, but instead of 6.0 parts of cyclopentane, 6.0 parts of trans- 1,2- dimethyl-cyclopropane.

Example 10 (in accordance with the invention)

The same as example 6, but instead of 6.0 parts of cyclopentane, 6.0 parts of cyclopentane, 6.0 parts of cis- 1,2- dimethyl- cyclopropane.

Table 1

| Example | Density in KG/m3 | Thermal conductivity in mW/mK, immediate | Deformation at 0.05 N/mm2 after 50,000 min in % |
|---|---|---|---|
| 1v | 24.8 | 20.8 | 2.2 |
| 2e | 25.0 | 20.3 | 1.9 |
| 3e | 20.8 | 20.8 | 1.8 |
| 4e | 24.0 | 20.9 | 1.9 |
| 5e | 24.2 | 20.9 | 1.7 |
| 6v | 29.8 | 24.0 | 2.5 |
| 7e | 29.5 | 23.5 | 1.2 |

| | | | |
|---|---|---|---|
| 8e | 29.9 | 23.8 | 1.1 |
| 9e | 29.6 | 24.0 | 1.4 |
| 10e | 29.5 | 24.1 | 1.3 |

e: example in accordance with the invention
v: comparative example

As compared to the known test samples foamed with cyclopentane, the foams in accordance with the invention exhibit significantly lower rates of deformation at lower rates of thermal conductivity as well, for example, due to the out-diffusing action of the foaming agents.

## Patent Claims

1. Process for the production of foam materials containing polyisocyanate - polyaddition products by transformation of (a) polyisocyanates, (b) versus isocyanate reactive compounds with a molecular weight of 500 to 8,000 g/mole and possibly (c) chain elongating agents and/or cross linking agents with a molecular weight of less than 500 g/mole in the presence of foaming agents (d) and of catalysts (e) as well as possibly of (f) auxiliary agents and additives, **thus characterized** in that foaming agents are used, containing hydrocarbons with $C_3$ or $C_4$ rings, exhibiting a boiling point between 0°C and 75°C at a pressure of 1,013 mbar.

2. Process in accordance with claim 1, thus characterized in that aliphatic cyclic compounds are used with $C_3$ or $C_4$ rings and with a total of 4 to 7 carbon atoms.

3. Process in accordance with claim 2, thus characterized in that foaming agents are used containing bicyclo [1.1.1] pentane, spiropentane, trans- 1,2- dimethyl- cyclopropane, cis- 1,2- dimethyl cyclopropane, 1- methyl bicyclo[1.1.0] butane, ethyl cyclopropane, methyl cyclobutane and/or bicyclo [2.1.0] pentane.

4. Process according to one of the claims 1 through 3, thus characterized in that foaming agents are used containing mixtures of hydrocarbons with $C_3$ or $C_4$ rings and compounds that are entirely or partially homogeneously miscible with these, exhibiting a boiling point between - 40°C and 100°C at a pressure of 1,013 mbar.

5. Process according to claim 4, thus characterized in that mixtures are used containing cyclopentane and/or highly fluorinated and/or perfluorinated hydrocarbons.

6. Process in accordance with one of the claims 1 through 5, thus characterized in that the foaming agent is used at a quantity of 0.5 to 25 weight percent relative to the weight of the component (b).

7. Components reacting to isocyanates, containing foaming agents for the production of foamed materials in accordance with claim 1 containing 5 to 25 weight percent hydrocarbons with $C_3$ or $C_4$ rings, which exhibit a boiling point between 0°C and 75°C at a pressure of 1,013 mbar as well as compounds which are possibly homogeneously miscible with the former with a boiling point between - 40°C and + 100°C at a pressure of 1,013 mbar, with 0.5 to 3 weight percent water and 82 to 94.5 weight percent of the component (b) and possibly of the component (c).

8. Foam materials containing polyisocyanate - polyaddition products, obtainable by a process in accordance with one of the claims 1 through 6.

9. Application of foamed materials in accordance with claim 8 as material for heat insulation in refrigerating and/or heating appliances, in sandwich elements or pipe lines.

10. Use of mixtures containing hydrocarbons with $C_3$ or $C_4$ rings, exhibiting a boiling point between 0°C and 75°C at a pressure of 1,013 mbar, for the production of foamed materials containing polyisocyanate - polyaddition products.